LEAD CARBONATE, A NEW FAST, HEAVY SCINTILLATOR

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Abstract

We describe the scintillation properties of lead carbonate ($PbCO_3$), a newly discovered, heavy (6.6 g/cm^3), inorganic scintillator. Its fluorescence decay lifetime, measured with the delayed coincidence method, is described by a sum of three exponentials; 24% of the light is emitted with a 5.6 ± 1 ns time constant, 48% of the light is emitted with a 27 ± 2 ns time constant, and 28% is emitted with a 155 ± 10 ns time constant. The emission spectrum peak is centered at a wavelength of 475 nm, and drops to less than 10% of its peak value at 370 nm and 580 nm. We have been unable to obtain an optical quality crystal of pure $PbCO_3$, but when a 3 mm cube of a cerussite (a naturally occurring mineral form of $PbCO_3$) is excited with 511 keV photons, a photopeak with a 42% full width at half maximum is observed at approximately 9% the light output of a bismuth germanate (BGO) crystal with similar geometry. The light output increases rapidly with decreasing temperature, plateauing at twice the light output of BGO at approximately -40° C. Lead hydroxide ($Pb(OH)_2$) can be mixed with $PbCO_3$ in a 1:2 ratio without significantly affecting the scintillation properties. The short fluorescence lifetime, high density, and reasonable light output of this new scintillator suggest that it would be useful for applications where high counting rates, good stopping power, and nanosecond timing are important, such as medical imaging and nuclear science.

1 Introduction

This paper describes the scintillation properties of lead carbonate ($PbCO_3$), a newly discovered inorganic scintillator. The physical characteristics of $PbCO_3$ are well suited for use as a gamma radiation detector. It has a density of 6.6 g/cm^3, is not hygroscopic, and is birefringent with indices of refraction of 1.80 and 2.08 [1]. The crystal structure is rhombic [1], its attenuation length for 511 keV photons is 1.1 cm, and it is colorless, transmitting wavelengths down to approximately 270 nm. We have been unable to obtain an optical quality synthetic crystal of pure lead carbonate, and therefore have performed our measurements using crystals cut from a naturally occurring mineral form of $PbCO_3$ known as cerussite. Also, all measurements were performed at room temperature (24° C) unless otherwise indicated.

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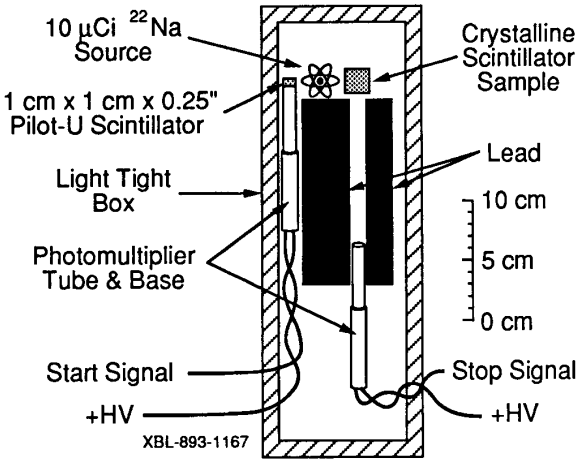

Figure 1: Delayed-Coincidence Apparatus

2 Fluorescent Decay Time

The fluorescent decay lifetime was measured using the delayed-coincidence method of Bollinger and Thomas [2], as modified by Moszyński and Bengtson [3]. A diagram of this set-up is shown in Figure 1. A piece of Pilot-U plastic scintillator coupled to a Hamamatsu R-2055 photomultiplier tube provided a start signal, and another quartz-windowed Hamamatsu R-2055 photomultiplier tube placed 13 cm away from the $PbCO_3$ sample provided the stop signal. A 10 μCi ^{22}Na source provided the 511 keV photon pairs that excited both the plastic scintillator and the scintillator sample. Timing signals from both photomultiplier tubes were generated using two channels of a Tennelec TC-454 constant fraction discriminator, and the time difference

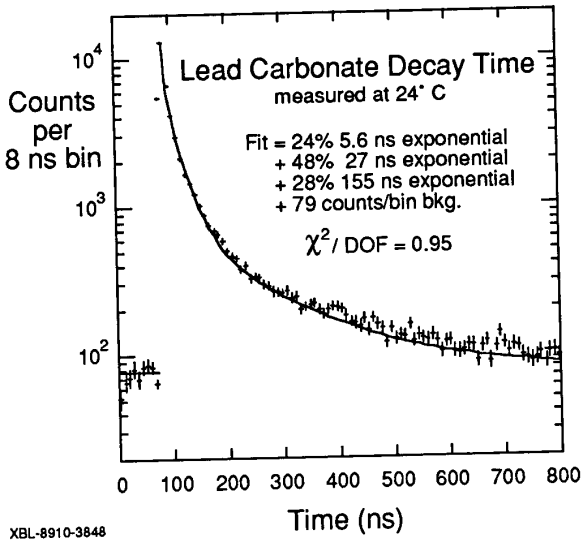

Figure 2: Fluorescence Decay Time of $PbCO_3$

between the start and stop signals was digitized with an Ortec 457 time to amplitude converter and a LeCroy 3512 analog to digital converter (ADC).

The results of this measurement are shown in Figure 2. A good fit to the data (the chi-squared per degree of freedom is 0.95) is obtained with a sum of three exponential decay lifetimes plus a constant background. Note that although the data Figure 2 is displayed in 8 ns bins, the data was acquired and fit using 0.4 ns bins. A significant fraction of the light (24% of the emitted photons) is produced with an 5.6 ± 1.0 ns decay constant, while 48% of the emitted photons are produced with a 27 ± 2 ns decay constant and 28% are produced with a 155 ± 10 ns time constant. The errors in this measurement are dominated by correlations between the three exponential terms.

3 Coincidence Timing

The coincidence resolving time of $PbCO_3$ was measured by exciting two crystals of $PbCO_3$, each coupled to a quartz windowed Hamamatsu R-2059 photomultiplier tube operated at -2500 V, with 511 keV photons resulting from positron annihilation from a ^{22}Na source placed between the two crystals. A timing signal from each photomultiplier tube was generated using two channels of a Tennelec TC-454 constant fraction discriminator, and the time difference between the two timing signals was digitized with an Ortec 457 time to amplitude converter and a LeCroy 3512 ADC. The resulting timing distribution, which has a FWHM of 1.3 ns and a full width at tenth maximum (FWTM) of 3.2 ns, is plotted in Figure 3. The same apparatus measures a timing distribution FWHM of 0.5 ns for Barium Fluoride (BaF_2).

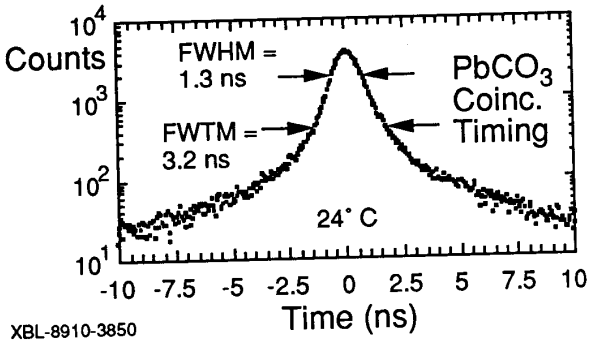

Figure 3: Coincidence Time Resolution

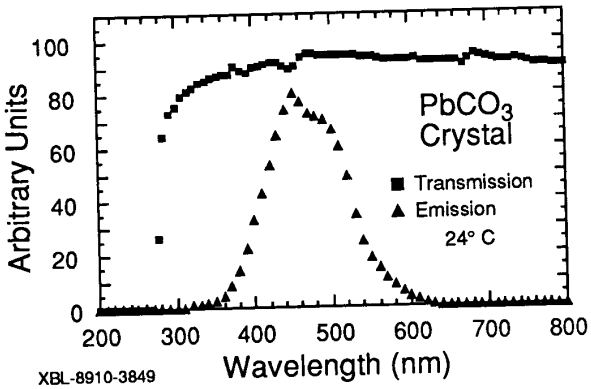

Figure 4: Emission and Transmission Spectra of $PbCO_3$

4 Emission Spectrum

The emission spectrum of $PbCO_3$ was obtained using a 0.125 meter Jarrell-Ash MonoSpec 18 monochromator with a 1200 line/mm grating blazed for 500 nm. The entrance and exit slits of this monochromator were 500 μm wide, resulting in a spectral resolution of 12 nm. The 511 keV photons from a 3.0 mCi ^{68}Ge source were used to excite a small (5 mm typical dimension) crystal that was cut from a cerussite crystal. The faces of this crystal were polished and covered on 5 sides with a reflective coating of white Teflon tape. The sixth side was placed at the entrance slit of the monochromator, and a quartz windowed Hamamatsu R-2055 photomultiplier tube (spectral range 200 nm to 600 nm) was placed at the exit slit. The resulting photomultiplier count rate is plotted, after background subtraction, as a function of monochromator wavelength in Figure 4. This spectrum is not corrected for the spectral response of the photomultiplier tube or monochromator. The emission spectrum peak is centered at 475 nm, and drops to 10% of its maximum intensity at 370 nm and 580 nm. Note that absence of light below the 300 nm cutoff of borosilicate glass implies that fused silica or UV glass windowed photomultiplier tubes are not necessary in order to collect all of the $PbCO_3$ scintillation light. The emis-

sion spectrum obtained with optical (254 nm) excitation is virtually identical to that obtained with 511 keV photon excitation.

Figure 4 also shows the transmission spectrum of a 3 mm thick sample of $PbCO_3$, as measured with a Shimadzu Spectronic 200UV spectrophotometer. The transmission is relatively uniform for wavelengths greater than 400 nm, with a gradual decrease between 400 nm and the ultimate cutoff of 270 nm, demonstrating that $PbCO_3$ is transparent to its own emissions. A small amount of structure is visible at 375 nm and near 450 nm – these structures are observed in several samples, but it is not clear what they are due to. The samples have been chemically analyzed and are almost entirely $PbCO_3$, but small amounts (<1%) of impurities may be present.

5 Light Output

The light output of $PbCO_3$ was measured by comparing its response to 511 keV photons to the response of a bismuth germanate (BGO) crystal under the same conditions. A 3 mm cube of cerussite was coated on five sides with a reflective coating of white Teflon tape, then optically coupled to a quartz-windowed Hamamatsu R-1306 photomultiplier tube with General Electric Viscasil 600M silicone fluid. The crystal was irradiated with 511 keV positron annihilation photons from a ^{22}Na source, and the output of the photomultiplier tube amplified with a Tennelec TC-222 amplifier with 1.2 μsec shaping time and digitized with a Lecroy 3512 ADC. The resulting pulse height spectrum is plotted (after pedestal subtraction) in Figure 5(a). The $PbCO_3$ crystal was removed and the same experiment was performed on a 3 mm cube of BGO, and the resulting spectrum is shown in Figure 5(b).

The photopeak corresponding to the 511 keV photon is seen in each plot in Figure 5. Note that the units used for the horizontal scale are the same for both plots. The 511 keV photopeak in $PbCO_3$ is centered at a pulse height that is 9% of the 511 keV photopeak pulse height in BGO. Using the BGO light output of 8200 photons/MeV reported by Holl, *et al.* [4], this implies that the light output of $PbCO_3$ is approximately 760 photons/MeV. The full width at half maximum (FWHM) in $PbCO_3$ of the 511 keV photopeak is 42%, which is consistent with a light output that is 9% of BGO.

The light output of $PbCO_3$ increases significantly when it is cooled. Figure 6 compares the light output of $PbCO_3$ at several temperatures to the light output of BGO at room temperature (24° C). The $PbCO_3$ light output at room temperature is 9% of BGO, exponentially increasing to twice that of BGO at approximately -40° C, and stabilizing at temperatures below -40° C. The ^{22}Na excited pulse height spectrum of cooled $PbCO_3$ is shown in Figure 5(c). Although we have not measured the effect of temperature on decay time, observation of oscilloscope traces indicates that the fast component of the decay time

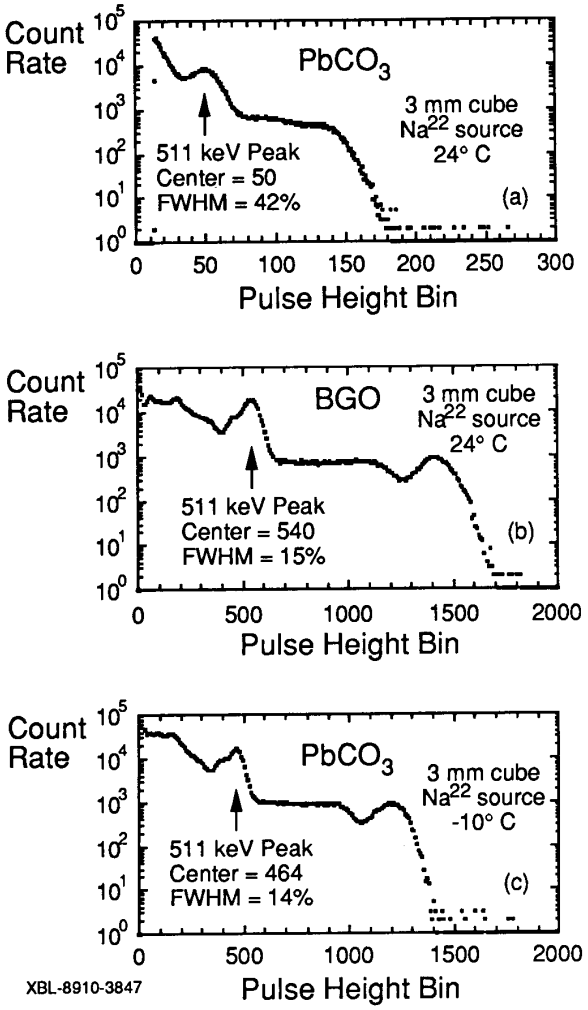

Figure 5: Light Output of (a) $PbCO_3$, (b) BGO, (c) cooled $PbCO_3$

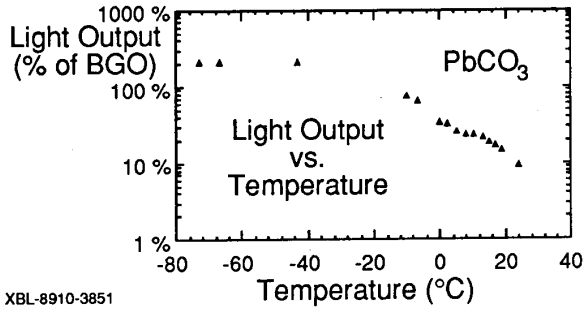

Figure 6: Light Output of $PbCO_3$ vs. Temperature

is not significantly changed as the temperature is reduced, but an additional slow ($\sim 1\mu s$) component is responsible for the increased light output.

6 Basic Lead Carbonate

Two molecules of lead carbonate can combine with a single molecule of lead hydroxide ($Pb(OH)_2$), to form a material known as basic lead carbonate, which has a density that is slightly less than pure $PbCO_3$ (6.2 g/cm^3). We have measured the scintillation properties of a powdered sample of pure basic lead carbonate, and found them to be very similar to those of cerussite crystals (*i.e.* pure $PbCO_3$). The fluorescence decay time of a powdered sample of basic lead carbonate was measured using the delayed coincidence method [2] on a sample excited with a 1 ns burst of 21.7 keV synchrotron x-rays from beamline X23-A2 at Brookhaven National Laboratory. The resulting spectrum is very similar to the distribution shown in Figure 2, and when fit with three exponentials as in Section 2, shows 32% of the photons emitted with an 6.6 ns decay time, 46% emitted with a 32 ns decay time, and 22% produced with a 138 ns time constant (χ^2/DOF = 1.1). The emission spectrum of the powdered sample was obtained by exciting the sample with synchrotron x-rays, then measuring the spectral output with the apparatus used to measure the emission spectrum of the cerussite crystal in Section 4. The resulting spectrum peaks at 480 nm, and has approximately the same width as the emission spectrum in Figure 4.

In addition, we checked powdered samples of lead hydroxide ($Pb(OH)_2$) for scintillation, and found that its scintillation light output is less than 1% of basic lead carbonate [5]. Since basic lead carbonate differs from pure $PbCO_3$ only by the addition of lead hydroxide and the scintillation properties of cerussite are very similar to those of basic lead carbonate, we therefore conclude that the $PbCO_3$ molecule is the active scintillator in both cerussite and basic lead carbonate and that the inclusion of lead hydroxide does not affect its scintillation properties. This also implies that the scintillation seen in the cerussite crystals is not caused by impurities in the crystal.

7 Synthetic Crystal Growth

As mentioned earlier, all measurements were made with crystals cut from a single naturally formed sample of $PbCO_3$, pictured in Figure 7. This sample has many black inclusions and internal cracks, which reduce the clarity of the crystal and lower its light collection efficiency. Therefore, the light output measurement is likely to be affected by the relatively poor optical quality of the cerussite crystal and the other measurements presented in this paper will probably not be affected. We hope that the light output presented here is a lower limit, and that the light output of this material will increase once it is learned how to grow optical quality single crystals of pure $PbCO_3$.

Figure 7: Photograph of the Cerussite Crystal
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Growing pure synthetic crystals is complicated because the decomposition temperature of $PbCO_3$ is lower than its melting point. However, it may be possible to grow optical quality crystals using a hydrothermal method, similar to the process used to grow single quartz crystals. Lead carbonate is slightly soluable in hot water, with its solubility increasing with increasing temperature. Therefore $PbCO_3$ is dissolved in 300° C water at approximately 1000 atmospheres pressure, and a 50° C temperature gradient is placed across this solution, forming $PbCO_3$ crystals at the colder end of the container [6].

It may also be possible to grow $PbCO_3$ crystals from the melt by driving the reverse of decomposition reaction. $PbCO_3$ breaks down into PbO and CO_2 when it is heated, so if it were heated under several thousand atmospheres of CO_2 pressure, the rate of the reverse of the decomposition reaction may increase enough to equal or exceed the decomposition rate. If this can be achieved, optical quality crystals can be grown using more conventional zone-refinement or Czochralski crystal growth techniques. This method has been applied with some success to grow optical quality $CaCO_3$ crystals [7].

8 Conclusions

Lead carbonate is a newly discovered, heavy, inorganic scintillator. Its density of 6.6 g/cm^3 is similar to that of

BGO (7.1 g/cm^3), and the attenuation length for 511 keV photons is the same as BGO (1.1 cm). Its fastest decay component (5.6 $\pm$ 1 ns) is slower than the 0.8 ns "fast" component of BaF_2, but considerably faster than BGO (300 ns) or the "slow" component of BaF_2 (620 ns). The $PbCO_3$ emission spectrum peak is centered at 475 nm, and so its emissions can be detected with good efficiency both by borosilicate glass photomultiplier tubes and PIN photodiodes. The scintillation light output is fairly low, approximately 9% of BGO at room temperature but increasing to twice that of BGO at -40° C. The light output measurements presented here were made with poor optical quality natural crystals, so we hope that the light output will be greater in synthetically grown pure $PbCO_3$ crystals. The scintillation properties are not appreciably affected when $Pb(OH)_2$ is added to form basic lead carbonate. It is unlikely that the scintillation is due to a trace impurity in this natural crystal, as similar scintillation properties are observed when a powdered sample of pure basic lead carbonate is excited with 22-keV X-rays.

The combination of high density, short fluorescence lifetime, and reasonable light output suggest that $PbCO_3$ would be useful for applications where high counting rates, good stopping power, and nanosecond timing are important, such as medical imaging and nuclear science. The absence of a significant "slow" fluorescent decay component implies that $PbCO_3$ would be well suited for applications where counting rates as high as 10 Mhz are expected.

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